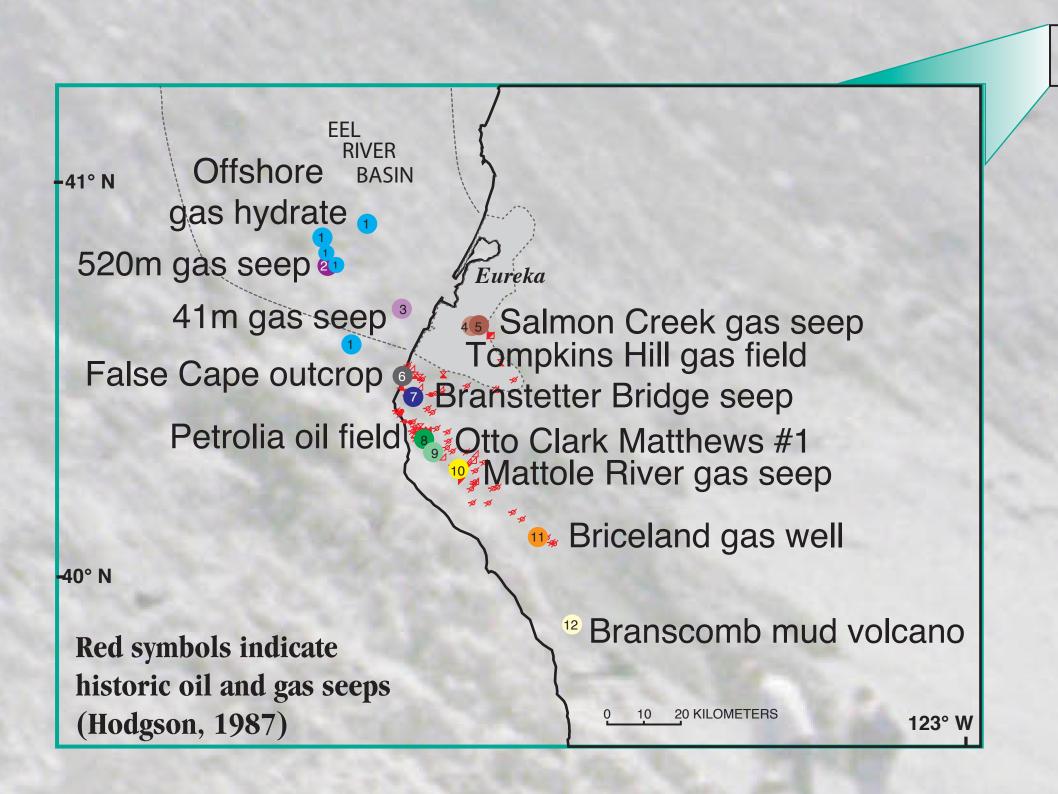


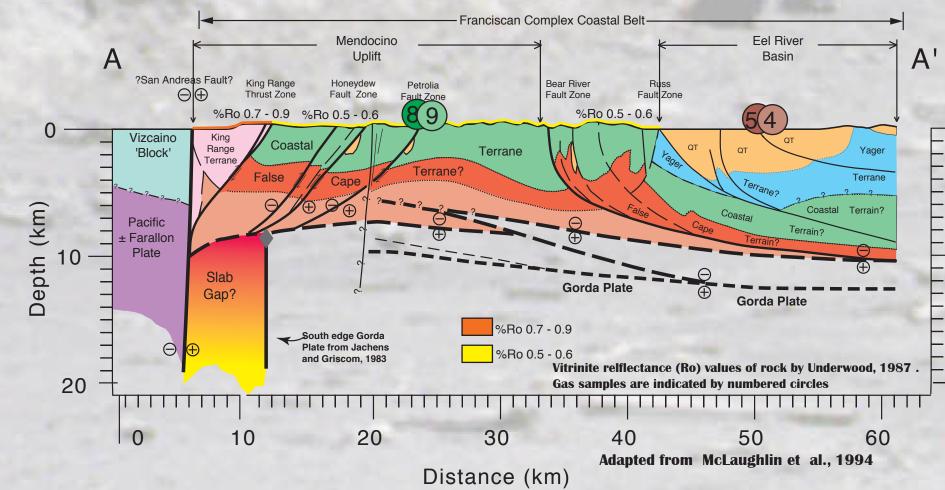
Comparison of Offshore and Onshore Gas Occurrences, Eel River Basin, Northern California

Monterey Bay Aguarium Research Institute

Introduction

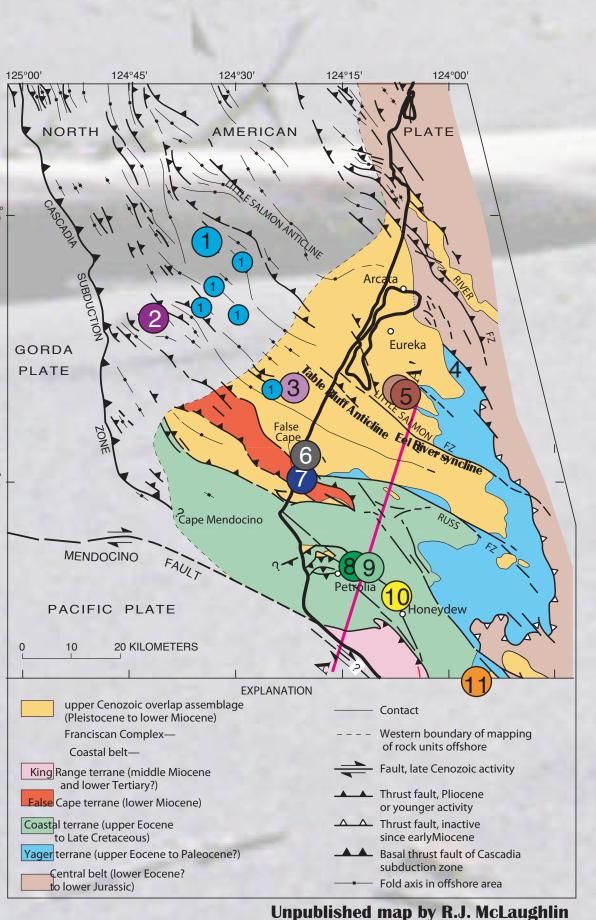
The Eel River basin of northern California is a upper Cenozoic depocenter containing more than 3,000 meters of sedimentary rock located near the Mendocino triple junction. Active tectonism has resulted in folding, faulting and rapid sedimentation. Both thermogenic and microbial hydrocarbons are known to be present in the sediments. In August 1997, we sampled two submarine gas seeps, one at a water depth of 520 m that supports a chemosynthetic-based ecosystem very near an area of previously recovered gas hydrate. Another vent site was sampled in sand covered with white bacterial mats at a water depth 41 m. We compared the hydrocarbon gas composition and methane isotopic composition of these seeps with land-based gas occurrences that include: 1) a gas seep and 2) gas from a 2360 m-deep gas well.





References:

no. 7, p.595-605.



Onshore Seeps

Analyses of the hydrocarbon gases from the onshore Salmon Creek seep and the Tompkins Hill gas field, show that the gas is about 96 to 98% methane with the remainder composed of higher molecular weight hydrocarbon gases at least up to heptane. In contrast to the mixed microbial-thermal source of the gases at the submarine gas seeps, the onshore gas seeps have molecular and isotopic compositions indicative of a thermal source: $C_1/(C_2+C_3)$ ratios are below 100; methane isotopic compositions are

-31.0 and -33.5% respectively. Other onshore gas occurrences to

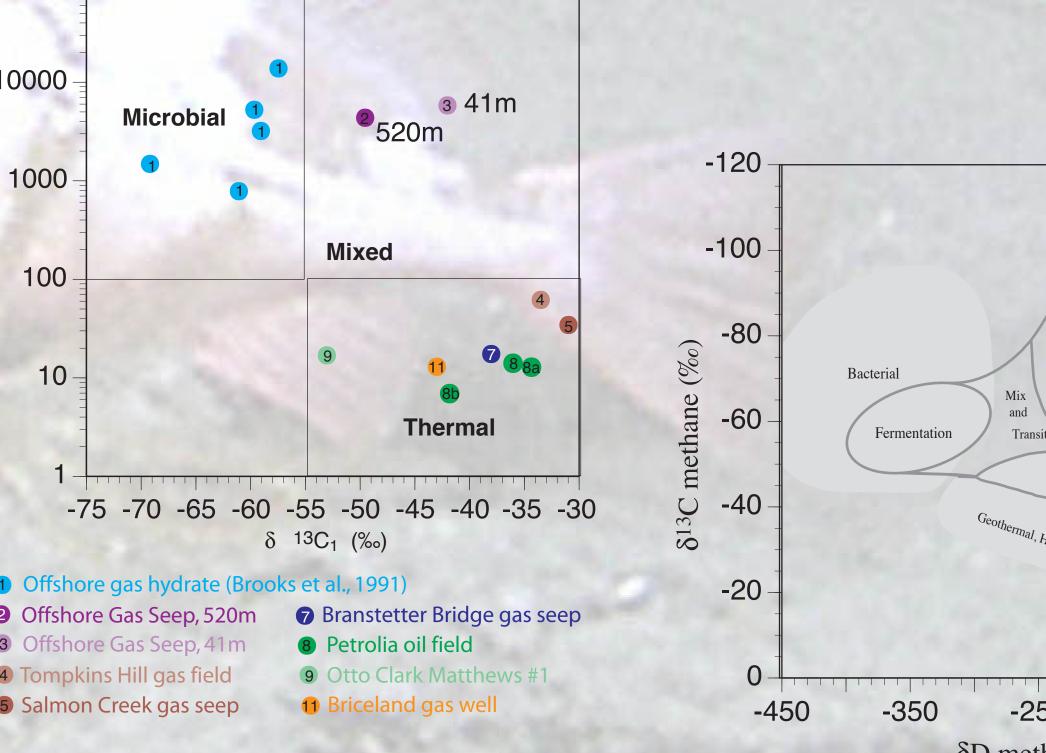
> the south have nearly identical molecular compositions to that of Tompkins Hill, however there is a divergence of methane isotopic

compositions. We think that the methane isotopic Branstetter Bridge values less than gas seep - 40% found

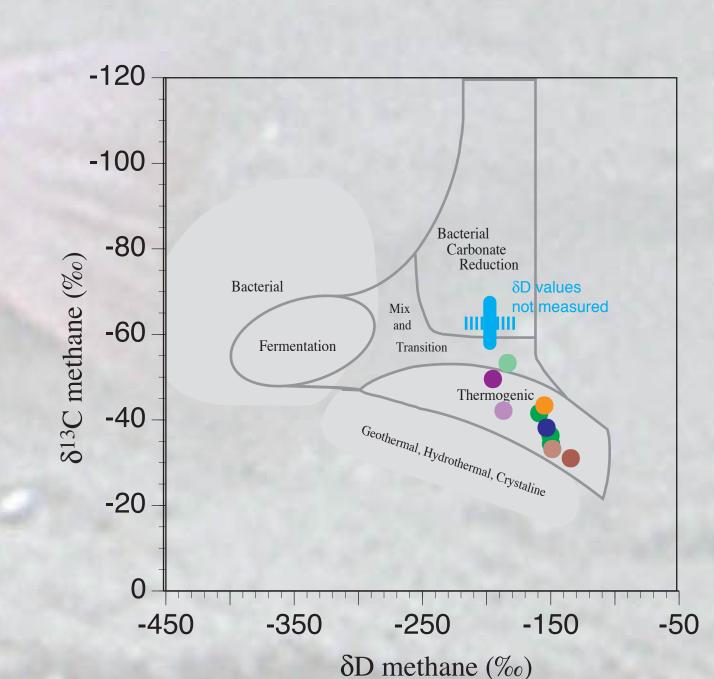
to the south are the result of fractionation during sampling. We conclude that all onshore gas occurrences stem from the same source.

Offshore Seeps

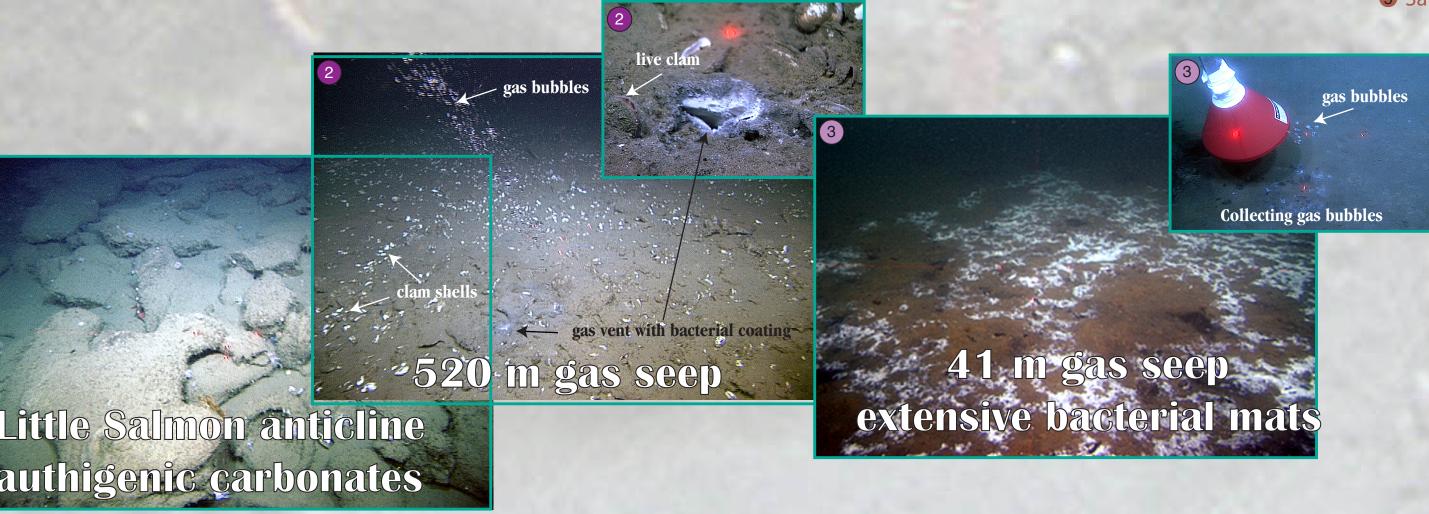
The offshore gas seeps (520m and 41m) are nearly 100% methane (C₁) with only 80 to 160 ppm ethane (C_2) and 13 to 9 ppm propane (C_3) respectively, 100000and $C_1/(C_2+C_3)$ ratios over 3500 suggesting a microbial methane source. Trace amounts of thermogenic gases, notably neopentane, 2,2dimethylbutane, and other branched hydrocarbons are present at both seeps, however these gases are much more abundant in concentration and variety at the 520-m seep. Carbon dioxide concentrations are less than 0.12% and hydrogen sulfide was not detected. The methane carbon isotopic composition of the 520-m and 41-m seep measured -49.5%, and -42.6%, respectively. These carbon isotopic compositions are unexpectedly heavy relative to the methane in gas hydrate (-59.6%) previously observed by Brooks et al., 1991 at the site of the 520 m seep. Analyses of the molecular and isotopic compositions of the submarine seep gases suggests that the gas currently escaping at the sea floor has a mixed thermogenic and microbial source.



Isotopic Analyses



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Geologic and Tectonic Setting

The southern Cascadia subduction margin just north of the Mendocino fracture zone is noteworthy for the west-northwestward trend of the folds and thrusts which characterize the accretionary complex and forearc area. This structural orientation results in the continuation and alignment of structures in the offshore area with those onshore in the region of the Mendocino triple junction (Clarke, 1992; McLaughlin and others, 1994) Gases sampled in the offshore and onshore Mendocino region, along with related petroleum and fluid seeps form a W-NW trend which roughly parallels the regional orientation of the thrusts and folds.

The onshore and offshore Mendocino region is underlain largely by accreted Mesozoic through Miocene rocks f the Franciscan Complex, and by Miocene and younger forearc or "overlap" strata of the Wildcat Group and Bear River beds of Ogle (1953). Accretionary rocks of the Franciscan Complex apparently merge westward in the offshore area with the modern accretionary complex associated with the active Cascadia subduction zone (Aalto et al., 1995; Clarke, 1992; McLaughlin et al., 1994). Onshore, rocks as young as Miocene are assigned to the Franciscan Complex (McLaughlin et al, 1982; Aalto et al., 1995; Underwood, 1989).

The Franciscan Complex may be further divided into three broad belts; the eastern, central and coastal; with rocks which generally become younger toward the western North American plate margin (Blake et al., 1988; McLaughlin et al., 1994). The belts are, in turn, subdivided into tectonstratigraphic terranes. The youngest of the belts of Franciscan rocks is the coastal belt, which largely consists of sandstone and shale of Eocene to middle Miocene age, and some minor blocks of Late Cretaceous basalt and pelagic limestone, derived from

Cape terranes (McLaughlin et al., 1994). These terranes of the coastal belt underlie the Cape Mendocino region. The Miocene King Range and False Cape terranes are of particular interest because the age of rocks in these terranes makes them source rock candidates and because gas and oil seeps issue from them.

The Eocene Coastal terrane is of interest mainly as an apparent fracture reservoir, but is apparently not a source for liquid petroleum or for the sampled gases. "Overlap" strata of the Wildcat Group and Bear River beds of Ogle(1953) overlie and are structurally interleaved with rocks of the Franciscan Complex along northeast and southwest-vergent thrusts. This relationship extends into the offshore accretionary margin. The interleaved imbricate relationship of Neogene "overlap" (forearc) strata with penetratively deformed Franciscan rocks, implies that the "overlap" strata must actually be structurally buried beneath Coastal belt Franciscan rocks along thrusts associated with the southern Cascadia subduction margin. This relationship partially explains the association of oil and gas seeps in Franciscan rocks of the Cape Mendocino region.

Aalto, K.R., McLaughlin, R.J., Carver, G.A., Barron, J.A., Sliter, W.V., and K. McDougall, 1995, Uplifted Neogene margin, southernmost Cascadia -Mendocino triple junction region, CA: Tectonics, V14, no.5, p.

Blake, M.C. Jr., Jacko, A.S., and McLaughlin, R.J., 1985, Tectonostratigraphic terranes of the northern Coast Ranges, California, in Howell, D.G. ed., Tectonostratigraphic terranes of the circum-Pacific region

Clarke, S.H. Jr., 1992. Geology of the Eel River basin and adjacent region: Implications for late Cenozoic tectonics of the southern Cascadia subduction zone and Mendocino triple junction. Am. Assoc.

McLaughlin, R.J., Kling, S.A., Poore, R.Z., McDougall, K.A., and Beutner, E.C., 1982, Post-middle Miocene accretioin of Franciscan rocks, northwestern California: Gological Survey of Americal Bulletin, v.93

McLaughlin, R.J., Sliter, W.V., Frederiksen, N.O., Harbert, W.P., and McCulloch, D.S., 1994, Plate motions redorded in tectonostratigraphic terranes of the Franciscan Complex and evolution of the Mendocino

Underwood, M.B., 1987. Thermal maturity and hydrocarbon potential of Franciscan terranes in coastal northern California: Accreted basement to the Eel River basin, in Schymiczek, H., and Suchland, R.,

Tectonics, sedimentation, and the evolution of the Eel River and other coastal basins of northern California: San Joaquin Geological Society Miscellaneous Publications, v. 37, p.89-98

Underwood, M.B., 1989, Temporal changes in goethermal gradient, Franciscan subduction complex, northern California: Journal of Geophysical Research, v.94 no. B3 p.3111-3125.

Brooks J. M., Field, M.E., and Kennicutt, M.C. II, 1991. Observations of gas hydrates in marine sediments, offshore northern California. Marine Geology 96: 103-109.

Iodgson, S.F., 1987. Onshore oil and gas seeps in California California Division of Oil and Gas publication No. TR26, Sacramento CA., 97 p.

Ogle, B.A., 1953, Geology of the Eel River Vallsy area, Humboldt County, California: California Division of Mines Bulletin 164, 128p.

(Earth Science Series, v. 1): Houston TX, Circum-Pacific Council for Energy and Mineral Resources, p. 159-171.

triple junction, northwestern California: U.S. Geological Survey Bulletin 1997, 60p.

Gas Analysis Results

normal butan

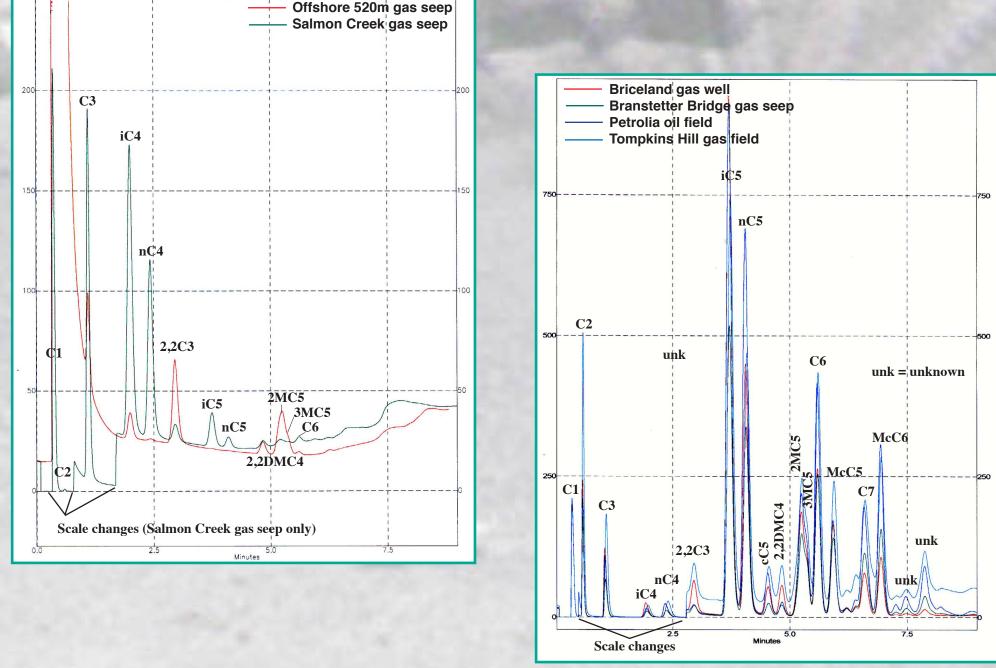
isopentane

McC5

normal pentane

methylcyclopentane

Location	date	O2+N2+A	r CO2 %	C1 ppm	C2 ppm	C2:1 ppm	C3 ppm	C3:1 ppm	iC4 ppm	nC4 ppm	2,2C3 ppm	iC5 ppm	nC5 ppm	c C5 ppm	2,2DMC4 ppm	2MC5 ppm	3MC5 ppm	C6 ppm	McC5 ppm	C7 ppm	McC6 ppm	C1/C2+C3	iC4/nC4	δ ¹³ C1	δ D C1	δ ¹³ C CO2
Eel River basin gas hydrate (Brooks et al., 1991)	1991	nr	nr	66-93%	100-1200		0-100	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	800-4700	nr	-57.6to-69	9.1 nr	nr
ERB 520 m gas seep area	8/26/97	0.32	0.11	995600	161.60	0.00	8.97	0.00	4.32	0.38	11.44	0.05	0.02	0.00	1.34	10.18	1.34	0.33	0.00	0.00	0.00	5837	11.25	-49.5	-196	-26.08
ERB 41.4 m gas seep area	8/25/97	67.1	0.00	328700	80.54	0.00	13.09	0.00	0.02	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3511	0.39	-42.6	-187	nd
Tompkins Hill Discovery Well	8/22/97	0.52	0.09	982800	10700	0.00	4130	0.00	640	890	12.70	197.00	112	16.13	15.37	91.80	20.48	93.45	66.49	81.32	84.70	66	0.72	-33.5	-149	nd
Salmon Creek gas seep	8/27/97	1.17	0.13	960300	26400	0.00	410	0.00	43.01	26.76	2.25	4.61	1.42	0.03	0.71	1.09	0.14	0.54	0.20	0.00	0.03	36	1.61	-31.0	-137	nd
False Cape outcrop	8/14/97	100	0.03	51.4	1.99	0.00	1.74	0.00	0.42	1.08	3.67	0.46	0.53	0.05	0.05	0.30	1.40	4.69	1.73	1.40	2.91	14	0.39	nd	nd	nd
Helen Branstedter Bridge (The eternal blue flame)	8/13/97	3.20	0.13	912000	35600	0.00	14800	0.00	3470	4280	35.42	1360	850	48.30	54.00	568	135	554	413	421	482	18	0.81	-38.4	-153	nd
Hidden Valley no. 1, API no. 023-20027 (Petrolia # 1) TD 1400'	8/15/97	2.51	0.78	882700	41600	0.00	23400	0.00	4750	7610	28.50	2370	1780	185	44.80	1150	194	938	551	763	990	14	0.62	-36.4	-151	nd
Shelby Woods no. 1, API no. 023-00097 (Petrolia # 2) TD 1538'	7 8/15/97	5.06	0.17	848200	40700	0.00	32000	0.00	8200	15800	6.81	679.00	573	86.90	16.69	407.0	103	504	270	310	290	12	0.52	-34.0	-158	nd
Whitchurch no. 1A, API no. 023-20065 (Petrolia #3) TD 2000'	8/15/97	7.01	0.72	790300	69200	0.00	43400	0.00	7060	9840	40.05	258.00	198	29.00	5.90	166	44.60	322	265	443	756	7	0.72	-42.0	-149	nd
Otto Clark Matthews #1 Petrolia	8/16/97	1.00	0.02	922000	29400	0.00	23500	0.00	5380	8572	11.80	3200	2150	288	24.60	1690	360	1400	408	1210	644	17	0.63	-53.6	-180	nd
Mattole River Gas seep	8/13/97	42.0	0.05	580000	90.00	0.00	9.08	0.00	0.52	0.00	0.04	0.11	0.00	0.00	0.04	0.18	0.11	0.05	0.13	0.26	0.23	5854		nd	nd	nd
Briceland gas well	8/12/97	0.65	0.08	901100	48100	0.00	25800	0.00	7180	7480	230	2320	1050	107	116	656	121	516	473	230	320	12	0.96	-43.0	-154	nd
Branscomb mud volcano	8/11/97	6.90	89.3	37700	149	0.00	23.00	0.00	3.05	4.40	0.20	1.07	0.77	0.19	0.03	0.31	0.08	0.36	0.30	0.19	0.30	219	0.69	nd	nd	-9.84
nr not reported nd not determined					100				-	100	100			-		-								-	1	750
C1 methane	20.	100		1	_		ore 520m ga on Creek gas																			



Comparison of Offshore and Onshore Gas Occurrences, Eel River Basin, Northern California Thomas D. Lorenson, Robert J. McLaughlin and Keith A. Kvenvolden (U. S. Geological Survey, Menlo Park, CA) Daniel L. Orange (University of California, Santa Cruz) M. Lee Davisson (Lawrence Livermore National Laboratories)

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of some thermal gas components with microbial methane generated at the seeps. Gas hydrate methane carbon isotopic composition previously measured in the offshore Eel River basin ranges from -57.6 to -69.1%Surprisingly, gas seeping from the offshore seeps are heavier than that of local gas hydrate. Five lines of evidence suggest that offshore gas is related to onshore thermal gas; 1. The geologic framework of the onshore and offshore are closely related, thus the likelyhood of the same petroleum system is good; 2. The hydrocarbon composition of the 520m gas seep site had some, but not all of the thermally-sourced higher molecular weight gas components present in the onshore gas samples; 3. The offshore seeps have carbon and deuterium isotopic compositions that are intermediate between Eel River basin gas hydrate and the thermal gases onshore; 4. The offshore gases have a distinct microbial overprinting. This explains the increased methane concentration in the offshore seeps, but does not account for the loss of higher molecular weight hydrocarbons if a simple mixing model is evoked. The microbial methane generated at the seeps are likely mixed with thermal gas; and 5. Carbon 14 was completely absent from the 520 m seep gas, thus the gas must come from depth where possible sources include thermogenic gas or deeply buried dissolved bicarbonate which has been out of contact with seawater carbonate sources for thousands of years.

Isotopic analyses of methane show that the gases are of

thermal or mixed origin. All onshore gases are of thermal

origin. The source of the offshore gas seeps is likely a mix

Chromatography

Gas chromatography shows that deep-seated gas occurrences on land, (Briceland gas well, Petrolia wells, Branstetter Bridge gas seep, and Tompkins Hill Discovery well) are all nearly identical in composition, implying a common source. The Salmon Creek seep (the closest natural seep to the offshore seeps) was compared to the Eel River basin 520 m deep seep with less correlation, and some components are missing in the 520 m seep site. The occurrence of trace amounts of thermogenic gases, notably neopentane, 2,2-dimethylbutane, and other branched hydrocarbons present at the 520 m seep site require some connection with a thermogenic source, likely the same source observed closeby on land.

Conclusions

- Onshore gas samples are of thermogenic origin and of similar composition suggesting a common hydrocarbon source.
- Onshore and offshore gas occur in similar geologic settings.
- Gas hydrate methane is mainly from a microbial source (Brooks et al., 1991).
- Offshore seeps are likely a mixture of microbial gas and modified thermogenic gas.

irm names is for descriptive purposes and does not imply endorsement by the U.S. Governme